INFLUENCE OF CERTAIN CATIONS ON THE INTENSITIES OF SPECTRAL EMISSIONS OBSERVED IN FLAME EXCITATION

by

ROBERT DUNNING WEAVER

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INTRODUCTION

This laboratory is interested in the development of analytical procedures for cations commonly present in plant material. The research presented here is the result of an investigation of the applicability of the flame spectrophotometric method to the determination of those cations. The cations studied were sodium, potassium, calcium, magnesium, iron, cobalt, copper, boron, and manganese. These elements are of botanical importance, their concentrations in plant material and in soils having been under extensive investigations to determine their relationship to the health and growth of plants (Beeson, 3).

Analysis of the alkali and alkaline earth metals by flame techniques has become an accepted method. Workers in the field, however, have reported the existence of interference which result in errors of analysis if unsuspected or uncorrected. It was the purpose of this investigation to discover such interferences between the cations mentioned above and their extent at concentrations expected in plant ash.

The instrument used was the Beckman Model DU Spectrophotometer with Model 9200 flame attachment. This instrument affords high resolution, is of low cost relative to spectrographic equipment, and is of widespread use.

SURVEY OF LITERATURE

Interferences in flame spectrophotometry have been observed by workers using different instruments. Barnes, et al. (1), in 1945, in describing a flame photometer of their own design which employed a Meker burner, stated that the presence of magnesium will alter results of calcium analysis. They also found that acids will decrease emission of sodium, lithium, potassium, and calcium, and that the presence of organic material may cause either a decrease or increase of emission. They showed that of the three anions, iodide, nitrate, and chloride, calcium emitted most strongly in the presence of the latter. Parks, et al. (12), using the Model 18 Perkin-Elmer flame photometer, found that large errors in results on alkali metals could be caused by the presence of the phosphate, borate, and oxalate ions. They showed that 1000 ppm of magnesium depressed emission caused by potassium and sodium. West, et al. (16), using the Beckman with the Model 10,300 attachment found sodium to increase results on potassium and calcium. Strohmeyer, et al. (15), using the Beckman Model DU with photomultiplier, found magnesium to depress calcium, but that calcium did not affect magnesium determinations. Kuemmel and Karl (9), using a Beckman Model DU with metal burner, found that individual ion interferences were negligible between sodium, lithium, calcium, magnesium, and others, but that the presence of phosphorous caused errors.

The use of flame photometry is expanding to analysis of metals other than those of the alkali and alkaline earth families. While there is not

yet extensive literature available for the other elements of interest in this work, there is some information to be found. The Beckman bulletin (Gilbert, 8), lists forty-six metals which may be detected by flame photometry. The analysis of lead in gasoline by flame methods has been used in the petroleum industry. Gerber, et al. (6) found, in a study of iron, cobalt, copper, and manganese, that iron and manganese interfere with cobalt. They found that analysis of copper and cobalt were unsatisfactory under the conditions employed. Applications of flame photometry to metals other than the alkalies are given in the bibliography of Noebels' paper (10).

Considerable work has been done to identify the causes of interference and either to eliminate them or reduce their effect. Many causes of interference in flame photometry are discussed in the literature, (2, 4, 5, 7, 9, 12, 13,) most of which are summarized by Gilbert, et al. (7), who list six types: 1) factors reducing flame temperature, 2) energy emitted at other wavelengths, 3) molecular emission, 4) adjacent line emission, 5) increase of background, and 6) alteration of rate of sample consumption. Porter and Wyld (13) divide interference into three groups: 1) overlapping spectra or background interference, 2) radiation interference, and 3) anion or acid interference.

It is generally felt that the magnitude and, at times, the occurrence of interference is dependent upon the type of instrument used and, among instruments of the same type, upon the particular instrument. It is to be expected that a flame photometer employing filters and a barrier-layer cell would exhibit greater interference and more occasions of

interference due to band emission and adjacent line emission than a refraction instrument employing photo-sensitive tubes. These considerations form the basis for the present investigation.

EXPERIMENTAL

Instrument and Apparatus

The Beckman Model DU Spectrophotometer is a single beam quartz prism photometer. A complete description may be found in the Beckman brochure (11). The phototube housing attached to the instrument was supplied with red and blue sensitive photo tubes. The blue sensitive tube was replaced with a photomultiplier tube and its necessary batteries and accessories (2).

The instrument dial is calibrated in units of percent transmittance (%T) and in optical density (log 1/T). Because of this calibration, results in flame photometry are usually presented in terms of percent transmittance; the expression "emission intensity" would, however, be more accurate. Because of the custom, and for the sake of convenience, the instrument readings observed in this research were recorded in units of percent transmittance.

The instrument parameters chosen were such that interferences due to band width and background were reduced to a minimum. Maximum electronic sensitivity was obtained by operation of the instrument with the sensitivity control knob near its extreme counter-clockwise limit. The number

of complete turns from the clockwise limit is listed under the heading of instrument parameters. Ten turns from the clockwise limit is the maximum.

To maintain optimum performance of the instrument, the batteries and desiccant were checked periodically and maintained at proper conditions. Increased humidity within the phototube housing due to a spent desiccant has caused erratic instrument behavior. A storage battery of lower than recommended specific gravity will change voltage during operation of the instrument causing dark current shift and consequent errors.

Maintenance of the burner itself was found to be of extreme importance. The temperature of the flame and the rate of sample consumption are the two major factors governing emission. The temperature of the flame with no aspiration of sample was maintained by accurately controlled gas pressures. The rate of sample consumption is not so easily controlled, being dependent upon the oxygen pressure, the position of the palladium capillary in relation to the oxygen jacket, the diameter of the capillary, and the viscosity of the sample.

The viscosity of dilute aqueous solutions of salts remains practically constant. Solutions of organic material or use of organic solvents may cause interference or a change in viscosity.

The centering of the capillary at the top of the burner is important. If the capillary is off center, the vacuum created by the passage of the oxygen is diminished, lowering the rate of sample consumption. Recentering may be accomplished by use of three positioning set screws within the burner. This procedure may be aided by using a twenty-power microscope.

The diameter of the capillary may change as scale is deposited, which has been observed with the aspiration of organic material and aqueous solutions containing calcium (Schrenk, 14). This scale may best be removed by aspirating warm dilute (1:10) hydrochloric acid.

A table was built for the spectrophotometer and all its flame attachments. The placement of the instrument was such that the operator, while seated, had easy access to sample bottles, instrument controls, the table switch panel controlling lights, battery charger and photomultiplier battery voltage supply, and the flame housing itself.

Experimental Procedures

The solutions used in this work were prepared from Baker and Adams analyzed reagents. The salts used were the chlorides or hydrated chlorides in all cases except iron, boron and calcium. Enough of the salt was added to one liter of distilled water to prepare a stock solution of 2000 ppm. Two grams of the cation are required for this concentration. In the case of calcium, calcium carbonate was used. This was allowed to react with just sufficient hydrochloric acid to prepare the chloride. Because of the hygroscopicity of the chlorides of iron, ferrous ammonium sulfate was used. Boric acid was employed for preparing standard boron solutions. All stock solutions were placed in polyethylene reagent bottles. Solutions kept in these bottles were unchanged after the lapse of one year's time.

To prepare a sample containing a given concentration of the ion desired,

the 2000 ppm stock was delivered from a burette into a two-ounce glass bottle. Water was then delivered to dilute to the desired concentration, bringing the final volume to thirty milliliters. The bottle was labeled and corked with a fresh, clean cork. The solution did not touch the cork and, in handling the bottle, effort was made to prevent contact of cork and solution. There are now available small glass bottles with polyethylene caps which would be desirable for this use. All glassware used, including the five-milliliter sample cups, was washed thoroughly with detergent, rinsed, placed in a stainless steel beaker filled with distilled water and placed on a steam bath for one hour or more. This leaching process is advisable to diminish the possibility of the dissolution of sodium from the glass into the sample solutions. Care must be taken when handling the glassware not to touch the surfaces of the glass near pouring lips, edges, etc., with the fingers (Schrenk, 1h).

During analysis of the solutions, the rate of consumption of four milliliters of water was timed with a stopwatch. Clogging and scaling could thus be detected.

When all solutions for analysis of a cation in the presence of another had been prepared, the instrument was turned on. The tube to be used was put into position and a warm up period of about one hour was usually allowed. The solution containing the highest concentration of the cation to be measured and containing no other cations was placed in the five-milliliter sample cup used in the flame sample holder. The burner was placed in operation using the oxygen and acetylene pressures recommended. The selector switch throughout this work was set at the 0.1

position. The dark current was adjusted and the slit opened to some value, usually 0.1 mm. With the sensitivity knob in the extreme counterclockwise limit, the sample cup was placed under the burner capillary. The wavelength knob was then turned to the wavelength recommended for the cation (Gilbert, 8) and adjusted about this value until the highest emission was obtained. This was indicated by the highest percent transmittance value required to restore the null reading of the galvanometer. During this process, it was usually necessary to change the slit width to keep the readings on scale. The wave length knob was left in the position yielding maximum response. This procedure was used each time the ion was re-investigated; thus small errors in wavelength calibration were avoided. The slit width knob was then adjusted to bring the percent transmittance reading close to that desired for the solution of highest concentration, usually 100 percent transmittance, and then adjusted to the next larger slit opening indicated on the slit width scale. This was done so that the setting could be accurately reproduced. Final balance to 100 percent transmittance was done with the sensitivity knob.

RESULTS

The interference data reported in this thesis were obtained with exclusive use of the photomultiplier tube. The recommended upper limit of the range of this tube is 600 mμ; however, the tube used was found to be serviceable at the principal wavelength of potassium emission, 768 mμ. Data were obtained to compare the red sensitive phototube and the photo-

multiplier at the wavelengths of sodium, calcium, and potassium. These data are presented in Table 1. and plotted in Figs. 1 through 3. The data indicate that much smaller slit widths were obtained with use of the photomultiplier as compared with the red tube. The sensitivity control knob was maintained at a setting of nine turns from the clockwise limit during operation of both tubes. The curves for potassium indicate decreased sensitivity while using the photomultiplier at the parameters listed. However, the slit width used with the photomultiplier was one-tenth that used for the red sensitive tube. The choice of the photomultiplier tube for calcium and potassium was made on this basis, because of the desire to use the smallest slit width possible.

Table 1. Comparison of phototubes.

Ion	Conc. ppm	0	10	12	60	100	Slit width
Na 589 mu	Red tube %T	2.5	29.2	32.1	73.5	90	1.0 mm
	Photomultiplier %T	1.3	30.6	32.1	74.5	90	0.01 mm
K 768 mu	Red tube %T	0.5	13.3	15.8	64.0	90	0.8 mm
	Photomultiplier %T	9.8	22.3	24.2	67.9	90	0.08 mm
Ca 622mu	Red tube %T	6.0	17.3	19.5	59.6	90	2.0 mm
	Photomultiplier %T	1.5	9.8	11.6	52.8	90	0.03 mm

Calibration data for each ion were obtained at the time the interference data for that ion were gathered. The highest concentration used in the calibration curve was greater than the highest concentration studied for interference. By this means, interferences causing elevation

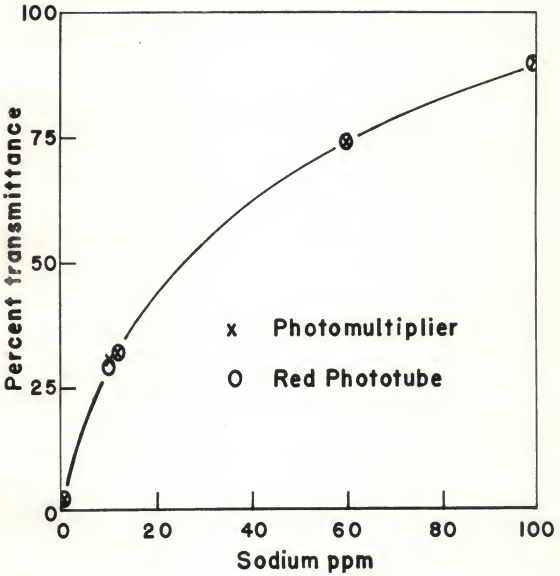

Fig. 1. Comparison of phototubes.

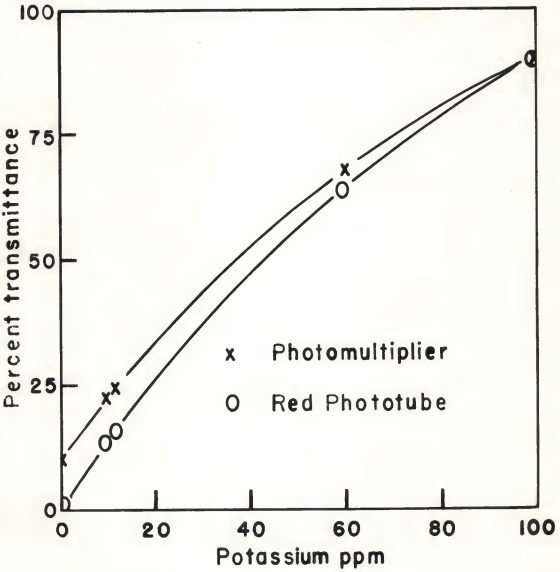

Fig. 2. Comparison of phototubes.

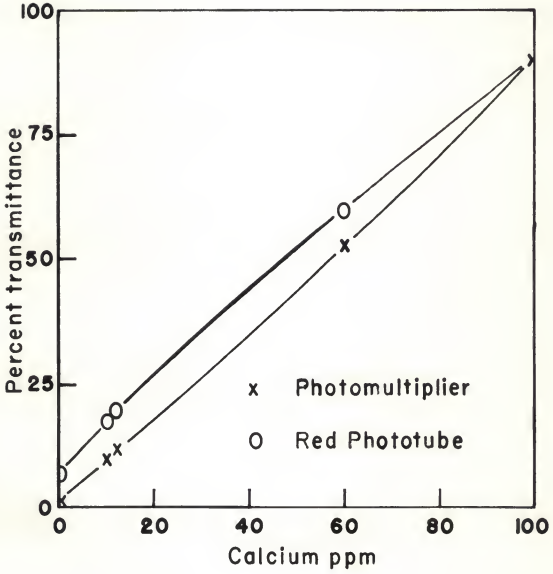

Fig. 3. Comparison of phototubes.

could be reported in concentration units.

The emission due to interference was, in some cases, larger than that due to the highest standard used. The results reported in these cases were obtained by linear extrapolation of the standard curve. Interference data thus obtained are preceded by an asterisk. Errors due to interference are reported in units of parts per million concentration change. The tables of calibration data and the curves for each ion precede the tables of observed interferences. Because of the great difference in the chemical nature and the concentration of sodium, potassium, calcium and magnesium, as compared with the rest of the cations considered, these were studied as a group and referred to as major elements, while the others are referred to as minor elements.

Because this investigation was intended to guide the later development of a method of analysis of botanically important elements, it was desired to study these elements at concentrations usually occurring in plant material. On the basis of the work by Beeson (3) the following table of concentrations to be expected in plant materials has been compiled.

Table 2. Concentration of elements.

Element	: Concentration ppm
Sodium	15,000
Potassium	20,000
Calcium	20,000
Magnesium	2,500
Iron	430
Manganese	75
Boron	27
Copper	10
Cobalt	0.1

The concentrations studied were based upon this table and exceeded these concentrations only in the case of the minor elements. The major element concentrations studied were based upon the assumption of a dilution factor of about twenty. As will be shown, the minimum concentration of cobalt studied was 2 ppm, which necessitates that a concentration of plant ash be performed for this analysis.

The Major Ions

The standard calibration curves and the data employed to obtain them are presented in Figs. 4 through 7, and in the paragraph below. The data for the interference between the major ions are presented in Tables 4 through 15. The interference data for each element, as affected by another of its group, are presented in separate tables. These tables are divided into four columns. The first column of each table presents the known concentrations of the ion under investigation. The second column lists the known concentrations of the ion which may cause interference. Column three presents the concentrations of the desired ion as determined by flame analysis. The fourth column presents the error in parts per million of the desired ion which is the difference between the known concentration and that determined by flame analysis.

Calibration data for sodium, potassium, calcium, and magnesium are:

Sodium:

Instrument parameters: wave length, 589 mu; slit width, 0.01 mm.; turns sensitivity knob, 8.

ppm Na	0	10	30	60	80	100	125	150	200
Avg. %T	0.5	25.5	44.9	60.9	70.4	75.8	84.4	90.1	100

Potassium:

Instrument parameters: wave length, 768 mu; slit width, 0.10 mm; turns sensitivity knob, 9.

ppm K	0	10	30	60	80	100	125
Avg. %T	12	26.4	45.3	66.4	79.8	88.4	100

Calcium:

Instrument parameters: wave length, 622 mu; slit width, 0.035 mm; turns sensitivity knob, 9.

ppm Ca	0	10	30	60	80	100	125
Avg. %T	2.3	10.9	24.7	45.1	62.0	81.1	100

Magnesium:

Instrument parameters: wave length, 371 mu; slit width, 0.04 mm; turns sensitivity knob, 9.

ppm Mg	0	100	200	300	400	500	600
Avg. %T	31	41.7	52.3	65.5	79.2	90.5	100

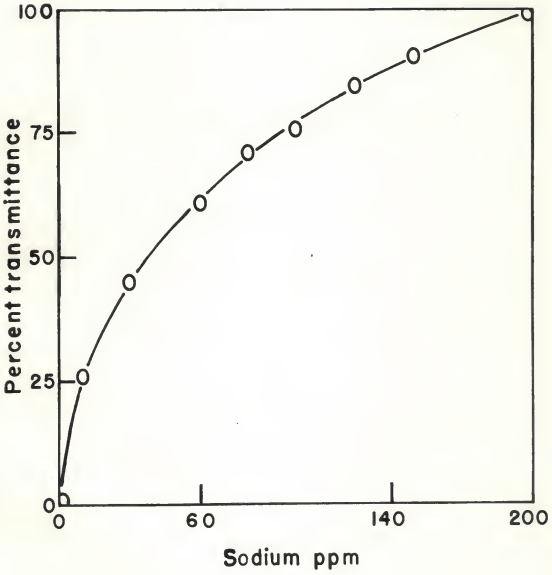

Fig. 4. Sodium calibration curve.

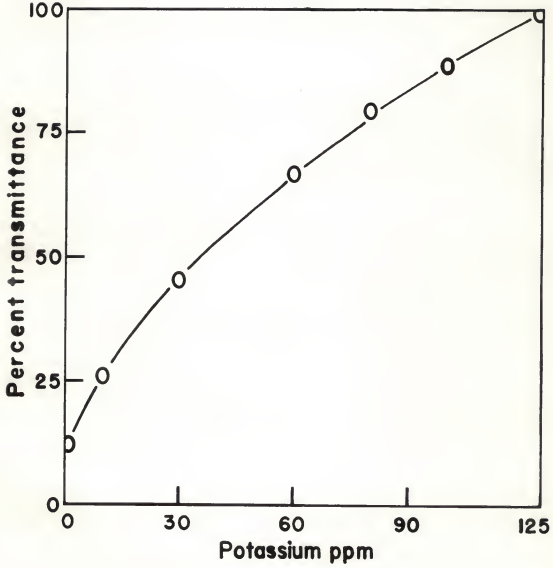

Fig. 5. Potassium calibration curve.

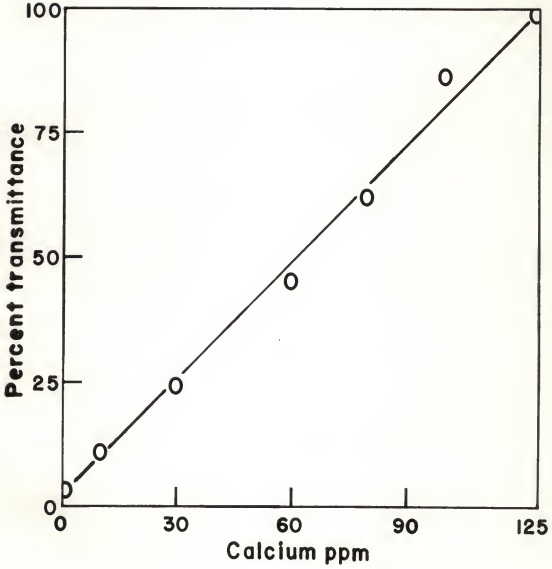

Fig. 6. Calcium calibration curve.

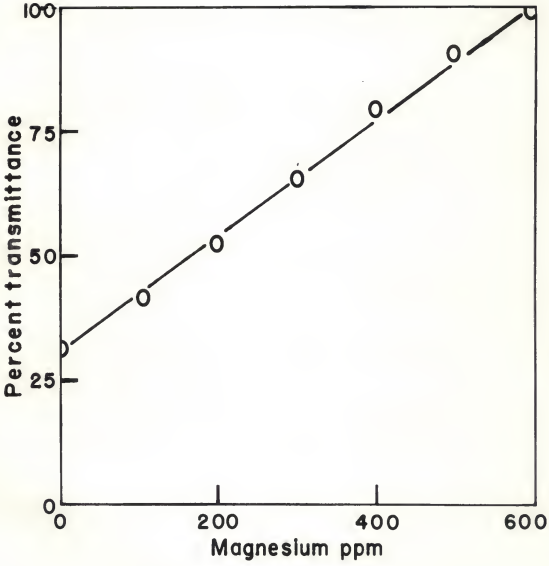

Fig. 7. Magnesium calibration curve.

Table 4. Effect of potassium on sodium.

Sodium Known P.P.M.	Potassium Known P.P.M.	Sodium Found P.P.M.	Error P.P.M.
0	0	0	0
0	10	1	1
0	60	1	1
0	100	1	1
0	200	1	1
10	0	10	0
10	10	10	0
10	60	10	0
10	100	10	0
10	200	10	0
60	0	60	0
60	10	62	2
60	60	65	5
60	100	66	6
60	200	70	10
100	0	100	0
100	10	100	0
100	60	104	4
100	100	106	6
100	200	110	10

Table 5. Effect of calcium on sodium.

Sodium Known P.P.M.	Calcium Known P.P.M.	Sodium Found P.P.M.	Error P.P.M.
0	0	0	0
0	10	1	1
0	60	2	2
0	100	2	2
0	200	2	2
10	0	10	0
10	10	11	1
10	60	12	2
10	100	12	2
10	200	13	3
60	0	60	0
60	10	63	3
60	60	66	6
60	100	66	6
60	200	66	6
100	0	100	0
100	10	98	-2
100	60	100	0
100	100	100	0
100	200	103	3

Table 6. Effect of magnesium on sodium.

Sodium Known P.P.M.	Magnesium Known P.P.M.	Sodium Found P.P.M.	Error P.P.M.
0	0	0	0
0	10	0	0
0	60	0	0
0	100	1	1
0	200	1	1
10	0	10	0
10	10	14	4
10	60	14	4
10	100	13	3
10	200	17	7
60	0	60	0
60	10	62	2
60	60	63	3
60	100	63	3
60	200	66	6
100	0	99	- 1
100	10	93	- 7
100	60	94	- 6
100	100	95	- 5
100	200	98	- 2

Table 7. Effect of sodium on potassium.

Potassium Known P.P.M.	Sodium Known P.P.M.	Potassium Found P.P.M.	Error P.P.M.
0	0	0	0
0	10	0	0
0	60	0	0
0	100	1	1
0	200	1	1
10	0	10	0
10	10	10	0
10	60	12	2
10	100	14	4
10	200	15	5
60	0	60	0
60	10	63	3
60	60	64	4
60	100	67	7
60	200	71	11
100	0	100	0
100	10	98	- 2
100	60	103	3
100	100	106	6
100	200	112	12

Table 8. Effect of calcium on potassium.

Potassium Known P.P.M.	Calcium Known P.P.M.	Potassium Found P.P.M.	Error P.P.M.
0	0	0	0
0	10	1	1
0	60	2	2
0	100	7	7
0	200	0	0
10	0	10	0
10	10	11	1
10	60	10	0
10	100	10	0
10	200	10	0
60	0	60	0
60	10	62	2
60	60	64	4
60	100	64	4
60	200	65	5
100	0	104	4
100	10	100	0
100	60	103	3
100	100	103	3
100	200	104	4

Table 9. Effect of magnesium on potassium.

Potassium Known P.P.M.	Magnesium Known P.P.M.	Potassium Found P.P.M.	Error P.P.M.
0	0	0	0
0	10	0	0
0	60	0	0
0	100	0	0
0	200	1	1
10	0	10	0
10	10	10	0
10	60	10	0
10	100	10	0
10	200	10	0
60	0	60	0
60	10	60	0
60	60	60	0
60	100	60	0
60	200	62	2
100	0	100	0
100	10	101	1
100	60	103	3
100	100	97	- 3
100	200	99	- 1

Table 10. Effect of sodium on calcium.

Calcium Known P.P.M.	Sodium Known P.P.M.	Calcium Found P.P.M.	Error P.P.M.
0	0	0	0
0	10	0	0
0	60	0	0
0	100	0	0
0	200	0	0
10	0	10	0
10	10	10	0
10	60	13	3
10	100	14	4
10	200	13	3
60	0	60	0
60	10	61	1
60	60	57	- 3
60	100	58	- 2
60	200	58	- 2
100	0	103	3
100	10	103	3
100	60	102	2
100	100	101	1
100	200	100	0

Table 11. Effect of potassium on calcium.

Calcium Known P.P.M.	Potassium Known P.P.M.	Calcium Found P.P.M.	Error P.P.M.
0	0	0	0
0	10	0	0
0	60	0	0
0	100	0	0
0	200	0	0
10	0	10	0
10	10	12	2
10	60	12	2
10	100	13	3
10	200	13	3
60	0	60	0
60	10	61	1
60	60	60	0
60	100	56	- 4
60	200	55	- 5
100	0	103	3
100	10	102	2
100	60	102	2
100	100	100	0
100	200	92	- 8

Table 12. Effect of magnesium on calcium.

Calcium Known P.P.M.	Magnesium Known P.P.M.	Calcium Found P.P.M.	Error P.P.M.
0	0	0	0
0	10	0	0
0	60	0	0
0	100	1	1
0	200	1	1
10	0	10	0
10	10	10	0
10	60	19	9
10	100	12	2
10	200	13	3
60	0	57	- 3
60	10	58	- 2
60	60	60	0
60	100	68	8
60	200	68	8
100	0	103	3
100	10	103	3
100	60	108	8
100	100	115	15
100	200	125	25

Table 13. Effect of sodium on magnesium.

Magnesium Known P.P.M.	Sodium Known P.P.M.	Magnesium Found P.P.M.	Error P.P.M.
0	0	0	0
0	100	5	5
0	300	5	5
0	500	--	--
0	1000	---	---
100	0	100	0
100	100	80	- 20
100	300	100	0
100	500	105	5
100	1000	130	30
300	0	300	0
300	100	305	5
300	300	300	0
300	500	300	0
300	1000	300	0
500	0	500	0
500	100	500	0
500	300	500	0
500	500	480	- 20
500	1000	435	- 65

Table 14. Effect of potassium on magnesium.

Magnesium Known P.P.M.	Potassium Known P.P.M.	Magnesium Found P.P.M.	Error P.P.M.
0	0	0	0
0	100	0	0
0	300	0	0
0	500	--	--
0	1000	--	--
100	0	100	0
100	100	95	- 5
100	300	105	5
100	500	100	0
100	1000	130	30
300	0	300	0
300	100	300	0
300	300	300	0
300	500	305	5
300	1000	305	5
500	0	500	0
500	100	500	0
500	300	500	0
500	500	500	0
500	1000	515	15

Table 15. Effect of calcium on magnesium.

Magnesium Known P.P.M.	Calcium Known P.P.M.	Magnesium Found P.P.M.	Error P.P.M.
0	0	0	0
0	100	10	10
0	300	10	10
0	500	--	--
0	1000	--	--
100	0	100	0
100	100	105	5
100	300	130	30
100	500	155	55
100	1000	180	80
300	0	300	0
300	100	285	- 15
300	300	310	10
300	500	330	30
300	1000	345	45
500	0	500	0
500	100	500	0
500	300	565	65
500	500	600	100
500	1000	630	130

The Minor Ions

In addition to investigating the interferences between the ions of the minor group, it was of interest to ascertain the minimum concentrations of these which might be determined within a certain limit under the conditions of this research. Statistical evaluation of the calibration data led to the following minimum ion concentrations determinable at a standard deviation of ten percent: boron, 14 ppm; cobalt, 12 ppm; copper, 6 ppm; iron, 23 ppm; and manganese, 2 ppm. The calibration curves and interference data for these minor ions are presented in Figs. 8 through 13 and Tables 17 through 36. These data are tabulated in the manner presented for the major ions.

Calibration data for the cations cobalt, copper, iron, boron, and manganese are:

Cobalt:

Instrument parameters: wave length, 352.7 mu; slit width, 0.13 mm.; turns sensitivity knob, 9.

ppm Co	0	2	10	20	30	40
Ave. %T		41.0	43.0	46.5	50	54.0

Copper:

Instrument parameters: wave length, 324.8 mu; slit width, 0.08 mm.; turns sensitivity knob, 9.

ppm Cu	0	2	10	20	30	40
Ave. %T		22.6	33.9	43.8	50	54.8

Iron:

Instrument parameters: wave length, 372.0 mu; slit width, 0.045 mm.; turns sensitivity knob, 9.

ppm Fe	100	200	300	400	500	600
Ave. %T	17.0	24.5	32.0	39.0	45.6	51.5

ppm Fe	700	800	1000	1200
Ave. %T	57.0	61.0	70.0	78.0

Boron:

Instrument parameters: wave length, 548 mu; slit width, 0.02 mm.; turns sensitivity knob, 9.

ppm B	5	15	25	40	50
Ave. %T	38.0	41.5	46.5	50	54.3

Manganese Range 800 to 1200 ppm.

Instrument parameters; wave length, 403.4 mu; slit width, 0.04 mm.; turns sensitivity knob, 8.

ppm Mn	800	1000	1200
Ave. %T	42.0	50.0	59.0

Manganese Range 15 to 300 ppm.

Instrument parameters: wave length, 403.4 mu; slit width, 0.09 mm.; turns sensitivity knob, 8.

ppm Mn	15	25	50	75	100	200	300
Ave. %T	24.0	25.5	29.0	32.5	36.0	50.0	65.0

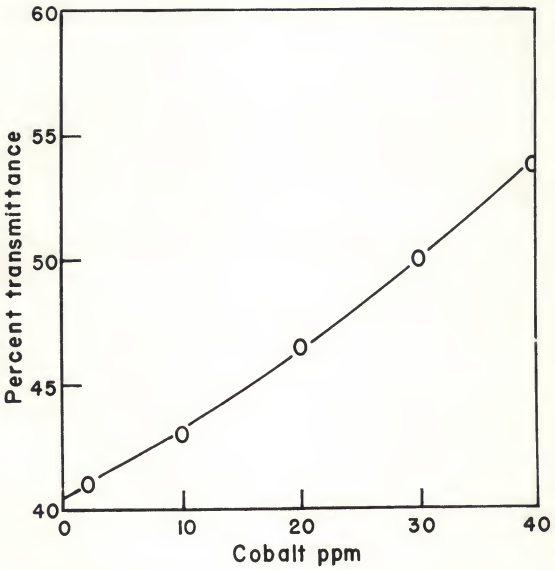

Fig. 8. Cobalt calibration curve.

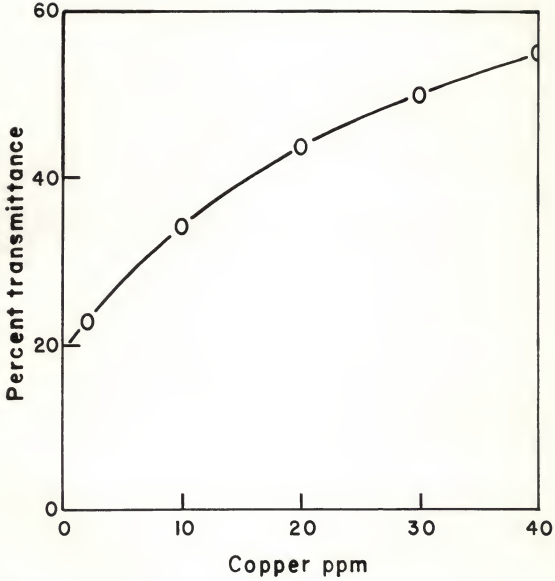

Fig. 9. Copper calibration curve.

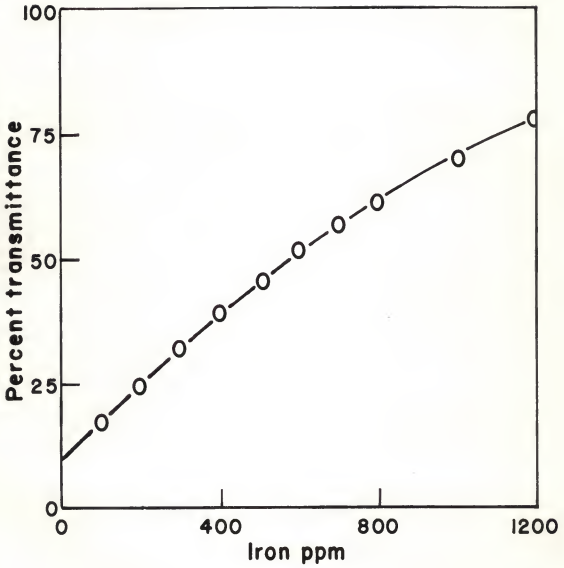

Fig. 10. Iron calibration curve.

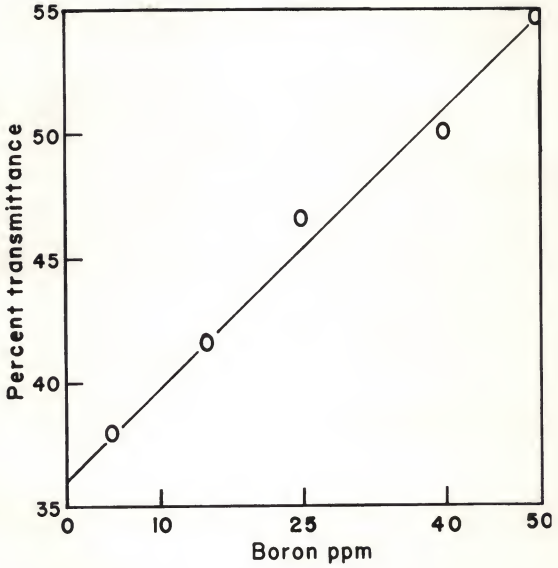

Fig. 11. Boron calibration curve.

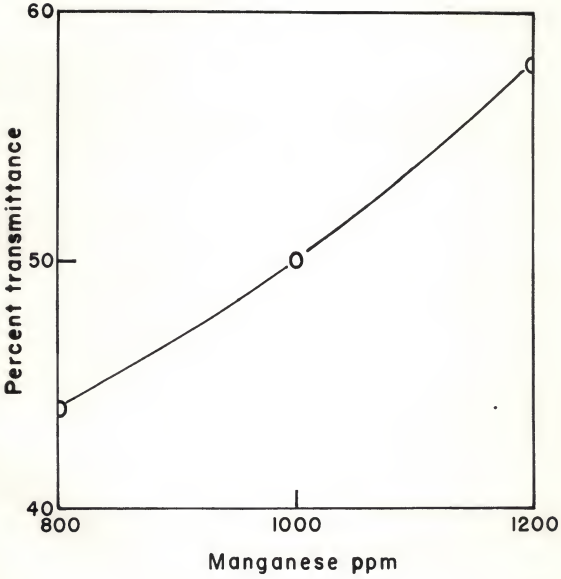

Fig. 12. Manganese calibration curve.

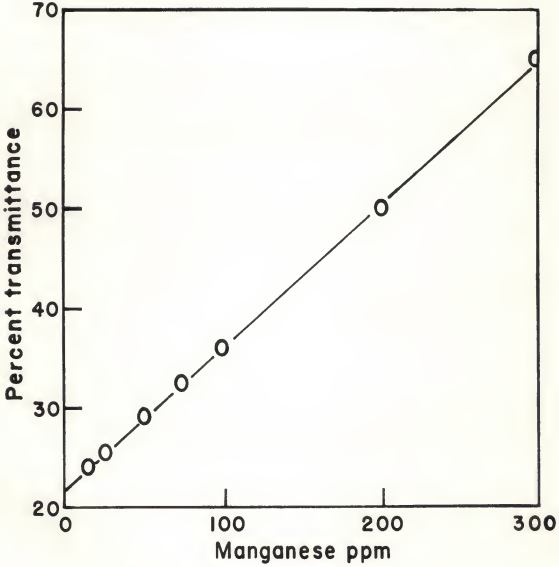

Fig. 13. Manganese calibration curve.

Table 17. Effect of cobalt on boron.

Boron Known P.P.M.	Cobalt Known P.P.M.	Boron Found P.P.M.	Error P.P.M.
5	2	4	- 1
5	10	4	- 1
5	20	5	0
5	30	6	1
15	2	15	0
15	10	10	- 5
15	20	14	- 1
15	30	15	0
25	2	24	- 1
25	10	24	- 1
25	20	29	4
25	30	26	1
40	2	37	- 3
40	10	40	0
40	20	42	2
40	30	41	1

Table 18. Effect of copper on boron.

Boron Known P.P.M.	Copper Known P.P.M.	Boron Found P.P.M.	Error P.P.M.
5	2	8	3
5	10	6	1
5	20	8	3
5	30	6	1
15	2	16	1
15	10	15	0
15	20	10	- 5
15	30	10	- 5
25	2	24	- 1
25	10	29	4
25	20	26	1
25	30	25	0
40	2	40	0
40	10	40	0
40	20	40	0
40	30	41	1

Table 19. Effect of iron on boron.

Boron Known P.P.M.	Iron Known P.P.M.	Boron Found P.P.M.	Error P.P.M.
5	200	62	57
5	400	*65	*60
5	600	*126	*121
5	1000	*>180	*>175
15	200	*78	*63
15	400	*142	*137
15	600	*200	*185
15	1000	*>180	*>165
25	200	*89	*64
25	400	*154	*129
25	600	*213	*188
25	1000	*>180	*>155
40	200	*95	*55
40	400	*157	*117
40	600	*236	*196
40	1000	*>180	*>140

Table 20. Effect of manganese on boron.

Boron Known P.P.M.	Manganese Known P.P.M.	Boron Found P.P.M.	Error P.P.M.
5	25	8	3
5	75	21	16
5	200	*60	*55
5	1000	*>175	*>170
15	25	24	9
15	75	37	22
15	200	*75	*60
15	1000	*>175	*>160
25	25	30	5
25	75	47	22
25	200	*85	*60
25	1000	*>175	*>150
40	25	43	3
40	75	*56	*16
40	200	*89	*49
40	1000	*>175	*>135

Table 21. Effect of boron on cobalt.

Cobalt Known P.P.M.	Boron Known P.P.M.	Cobalt Found P.P.M.	Error P.P.M.
2	5	4	2
2	15	4	2
2	25	4	2
2	40	4	2
10	5	10	0
10	15	10	0
10	25	10	0
10	40	10	0
20	5	20	0
20	15	20	0
20	25	20	0
20	40	20	0
30	5	30	0
30	15	30	0
30	25	30	0
30	40	30	0

Table 22. Effect of copper on cobalt.

Cobalt Known P.P.M.	Copper Known P.P.M.	Cobalt Found P.P.M.	Error P.P.M.
2	2	4	2
2	10	4	2
2	20	4	2
2	30	4	2
10	2	13	3
10	10	15	5
10	20	15	5
10	30	16	6
20	2	20	0
20	10	20	0
20	20	20	0
20	30	22	2
30	2	30	0
30	10	30	0
30	20	30	0
30	30	30	0

Table 23. Effect of iron on cobalt.

Cobalt Known P.P.M.	Iron Known P.P.M.	Cobalt Found P.P.M.	Error P.P.M.
2	200	16	14
2	400	26	24
2	600	36	34
2	1000	*70	*68
10	200	22	12
10	400	30	20
10	600	*57	*47
10	1000	*73	*63
20	200	29	9
20	400	39	19
20	600	*65	*45
20	1000	*79	*59
30	200	40	10
30	400	*66	*36
30	600	*77	*47
30	1000	*99	*69

Table 24. Effect of manganese on cobalt.

Cobalt Known P.P.M.	Manganese Known P.P.M.	Cobalt Found P.P.M.	Error P.P.M.
2	25	6	4
2	75	11	9
2	200	16	14
2	1000	*66	*62
10	25	11	1
10	75	15	5
10	200	22	12
10	1000	*71	*61
20	25	20	0
20	75	23	3
20	200	33	13
20	1000	*91	*71
30	25	30	0
30	75	32	2
30	200	40	10
30	1000	*97	*67

Table 25. Effect of boron on copper.

Copper Known P.P.M.	Boron Known P.P.M.	Copper Found P.P.M.	Error P.P.M.
2	5	3	1
2	15	3	1
2	25	3	1
2	40	3	1
10	5	9	- 1
10	15	9	- 1
10	25	9	- 1
10	40	9	- 1
20	5	20	0
20	15	19	- 1
20	25	19	- 1
20	40	18	- 2
30	5	28	- 2
30	15	29	- 1
30	25	29	- 1
30	40	29	- 1

Table 26. Effect of cobalt on copper.

Copper Known P.P.M.	Cobalt Known P.P.M.	Copper Found P.P.M.	Error P.P.M.
2	2	2	0
2	10	2	0
2	20	2	0
2	30	2	0
10	2	9	- 1
10	10	9	- 1
10	20	10	0
10	30	10	0
20	2	19	- 1
20	10	19	- 1
20	20	19	- 1
20	30	20	0
30	2	31	1
30	10	32	2
30	20	30	0
30	30	32	2

Table 27. Effect of iron on copper.

Copper Known P.P.M.	Iron Known P.P.M.	Copper Found P.P.M.	Error P.P.M.
2	200	3	1
2	400	3	1
2	600	4	2
2	1000	4	2
10	200	9	- 1
10	400	10	0
10	600	10	0
10	1000	11	1
20	200	20	0
20	400	21	1
20	600	22	2
20	1000	23	3
30	200	31	1
30	400	32	2
30	600	34	4
30	1000	38	8

Table 28. Effect of manganese on copper.

Copper Known P.P.M.	Manganese Known P.P.M.	Copper Found P.P.M.	Error P.P.M.
2	25	3	1
2	75	3	1
2	200	3	1
2	1000	3	1
10	25	9	- 1
10	75	10	0
10	200	10	0
10	1000	11	1
20	25	19	- 1
20	75	20	0
20	200	20	0
20	1000	22	2
30	25	28	- 2
30	75	28	- 2
30	200	29	- 1
30	1000	32	2

Table 29. Effect of boron on iron.

Iron Known P.P.M.	Boron Known P.P.M.	Iron Found P.P.M.	Error P.P.M.
200	5	200	0
200	15	200	0
200	25	200	0
200	40	200	0
400	5	400	0
400	15	400	0
400	25	400	0
400	40	400	0
600	5	580	- 20
600	15	580	- 20
600	25	600	0
600	40	580	- 20
1000	5	1010	10
1000	15	1000	0
1000	25	990	- 10
1000	40	1000	0

Table 30. Effect of cobalt on iron.

Iron Known P.P.M.	Cobalt Known P.P.M.	Iron Found P.P.M.	Error P.P.M.
200	2	200	0
200	10	200	0
200	20	190	- 10
200	30	190	- 10
400	2	400	0
400	10	400	0
400	20	400	0
400	30	400	0
600	2	620	20
600	10	620	20
600	20	630	30
600	30	620	20
1000	2	990	- 10
1000	10	970	- 30
1000	20	970	- 30
1000	30	1000	0

Table 31. Effect of copper on iron.

Iron Known P.P.M.	Copper Known P.P.M.	Iron Found P.P.M.	Error P.P.M.
200	2	190	- 10
200	10	190	- 10
200	20	190	- 10
200	30	190	- 10
400	2	410	10
400	10	410	10
400	20	410	10
400	30	410	10
600	2	-	-
600	10	600	0
600	20	620	20
600	30	600	0
1000	2	970	- 30
1000	10	1000	0
1000	20	970	- 30
1000	30	980	- 20

Table 32. Effect of manganese on iron.

Iron Known P.P.M.	Manganese Known P.P.M.	Iron Found P.P.M.	Error P.P.M.
200	25	210	10
200	75	210	10
200	200	220	20
200	1000	320	120
400	25	410	10
400	75	410	10
400	200	430	30
400	1000	500	100
600	25	620	20
600	75	620	20
600	200	630	30
600	1000	710	110
1000	25	1000	0
1000	75	970	- 30
1000	200	1000	0
1000	1000	1120	120

Table 33. Effect of boron on manganese.

Manganese Known P.P.M.	Boron Known P.P.M.	Manganese Found P.P.M.	Error P.P.M.
25	5	35	10
25	15	40	15
25	25	40	15
25	40	50	25
75	5	75	0
75	15	80	5
75	25	85	10
75	40	90	15
200	5	200	0
200	15	210	10
200	25	220	20
200	40	225	25
1000	5	1070	70
1000	15	1070	70
1000	25	1070	70
1000	40	1020	20

Table 34. Effect of cobalt on manganese.

Manganese Known P.P.M.	Cobalt Known P.P.M.	Manganese Found P.P.M.	Error P.P.M.
25	2	25	0
25	10	25	0
25	20	25	0
25	30	25	0
75	2	75	0
75	10	75	0
75	20	80	5
75	30	80	5
200	2	200	0
200	10	200	0
200	20	200	0
200	30	200	0
1000	2	995	- 5
1000	10	1005	5
1000	20	1005	5
1000	30	1030	30

Table 35. Effect of copper on manganese.

Manganese Known P.P.M.	Copper Known P.P.M.	Manganese Found P.P.M.	Error P.P.M.
25	2	25	0
25	10	25	0
25	20	25	0
25	30	25	0
75	2	70	- 5
75	10	70	- 5
75	20	70	- 5
75	30	70	- 5
200	2	200	0
200	10	200	0
200	20	200	0
200	30	200	0
1000	2	1020	20
1000	10	1020	20
1000	20	1010	10
1000	30	1020	20

Table 36. Effect of iron on manganese.

Manganese Known P.P.M.	Iron Known P.P.M.	Manganese Found P.P.M.	Error P.P.M.
25	200	110	85
25	400	190	165
25	600	260	235
25	1000	*392	*367
75	200	160	85
75	400	240	165
75	600	*320	*245
75	1000	*460	*385
200	200	270	70
200	400	*353	*153
200	600	*426	*226
200	1000	*560	*360
1000	200	1080	80
1000	400	1110	110
1000	600	1180	180
1000	1000	--	--

DISCUSSION

The analytical errors reported may be considered as being of two kinds; those due to interferences occurring in the flame, and errors due to variation of the instrument. The first type is related to the concentration of the interfering ion, while the second is nearly constant and independent of concentration.

The instrument parameters chosen for this research resulted in relatively high instrument variation. The use of the narrow slit width reduced the interference due to background and adjacent spectral lines to a minimum, but necessitated the use of maximum electrical sensitivity. These two factors, narrow slit width and high sensitivity, greatly increased the fluctuation of the galvanometer needle. It became difficult, therefore, to read the instrument with precision. However, duplicate readings of the null point seldom exceeded plus or minus one percent of the transmittance scale.

Porter and Wyld (13), for practical analytical purposes consider interferences occurring in the flame as being due to three factors. These are: overlapping of spectral lines or oxide bands, radiation interference, and anion interference. The latter is unlikely to be present in these data because of the principle use of chloride as the anion.

The interference of calcium with magnesium at 371 mu is probably due to overlapping of the line emission of calcium in this region with the oxide band emission of magnesium. The interference of magnesium with calcium is probably due to radiation interference since magnesium

does not emit appreciably at the calcium wave length of 622 mu. No interference above instrumental variation was observed for the rest of the ions of the major group. While interferences have been reported (1, 9, 12, 15, 17) for the other major elements, the lack of interference in these data may be attributed to the specific choice of conditions which minimized the occurrence of interferences.

Of the ions in the minor group, mutual interference was observed between iron and manganese. Iron is known to emit a large number of lines, even under conditions of low exitation energy. It is not surprising, therefore, to find an iron line near the wave length employed for manganese analysis. Thus the interference of iron with manganese may be attributed to overlapping spectral lines. The wave length used for iron analysis, 372 mu, is in a region of band emission for manganese. Therefore, interference of manganese with iron may be ascribed to background of band emission.

Boron was found to elevate results of manganese determinations. Boron emission is low at the wave length used for manganese, so this interference probably should be ascribed to radiation effects.

Interference was not observed between the rest of the minor ions. The specific choice of instrument parameters designed to reduce interference is, again, probably responsible.

On the basis of the foregoing discussion, the following interpretation of data is presented in Table 37. This table shows, in a qualitative manner, the occurrences of interferences between the ions included in this study. Interference is indicated by the use of the asterisk.

A single asterisk signifies interference observed above instrumental variation. Two asterisks indicate interference of considerable magnitude. A dash indicates no interference above instrument variation.

While quantitative data on interferences are presented for both major and minor ions, these data should not be used as corrections for interference observed in a flame analysis. Because of the nature of interferences, the quantitative data presented should be employed only as a guide in preparing standards and in interpreting results of preliminary analysis of an unknown sample. Exact correction for interference should be determined with the instrument and solutions to be used in the analysis.

Table 37. Interference of ions.

Interfering ion	Desired ion: Sodium	Potassium	Calcium	Magnesium
Sodium		--	--	--
Potassium	--		--	--
Calcium	--	--		**
Magnesium	--	--	*	

	Boron	Cobalt	Copper	Iron	Manganese
Boron		--	--	--	*
Cobalt	--		--	--	--
Copper	--	--		--	--
Iron	**	**	--		**
Manganese	**	**	--	**	

CONCLUSIONS

Interference was found to be mutually present between calcium and magnesium in the major group and between iron and manganese in the minor group. Interference of boron with manganese was also found. From these findings, it may be stated that analysis of plant ash, properly diluted, could be performed without regard for interference effects other than those noted, provided the separation of the constituents into the major and minor groups was first performed. It would be best to separate iron and manganese still further from the ions of the minor group, leaving a solution of cobalt, copper, and boron to be concentrated and analyzed separately.

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LITERATURE CITED

(1) Barnes, R. B., D. Richardson, J. W. Berry, and R. L. Hood. Flame photometry. A rapid analytical procedure. Ind. Eng. Chem. Anal. Ed. 17:605-611. 1945.

(2) Beckman Flame spectrophotometer. Bulletin 167-F, Dec. 1950.

(3) Beeson, Kenneth C.
The mineral compostion of crops with particular reference to the soils in which they were grown. A reveiw and compilation. United States Department of Agriculture Miscellaneous Publication 369. Washington, March, 1941.

(4) Bills, Charles E., Francis G. McDonald, William Niedermeier, and Melvin C. Schwartz.
Reduction of error in flame photometry. Anal. Chem. 21:1076, 1949.

(5) Conrad, A. L., and W. C. Johnson.
Flame photometer techniques. Anal. Chem. 22:1530-1533, 1950.

(6) Gerber, C. R., N. H. Ishler, and E. Borker.
Determination of iron, manganese, copper, and cobalt by the flame photometer. Anal. Chem. 23:684, 1951.

(7) Gilbert, P. T., Jr., R. C. Hawes, and A. O. Beckman.
Beckman flame spectrophotometer. Anal. Chem. 22:772-780, 1950.

(8) Gilbert, Paul T., Jr.
Flame photometry -- new precision in elemental analysis. Beckman reprint R-56, originally published in Industrial Laboratories, Aug., 1952.

(9) Kuemmel, J. F., and H. L. Karl.
Flame photometric determination of alkali and alkaline earth elements in cast iron. Anal. Chem. 26:386-391, 1954.

(10) Noebels, Henry J.
Applications of flame photometry. Beckman Reprint R-60.

(11) Operating instructions. Beckman bulletin 91-C, Nov., 1950.

(12) Parks, Thomas D, Hilton O. Johnson, and Louis Lykken.
Errors in the use of a model 18 Perkin-Elmer flame photometer for the determination of alkali metals. Anal. Chem. 20:822, 1948.

(13) Porter, Paul, and Garrard Wyld.
Elimination of interferences in flame photometry. Anal. Chem. 27:733-736, May, 1955.

(14) Schrenk, W. G., moderator.
Flame photometry, round table discussion. Anal. Chem. 22: 1202, 1950.

(15) Strohmeyer, F. B., B. E. Leach, and R. G. Heath.
Flame photometric determination of calcium and magnesium. Anal. Chem. 25:1935. 1953.

(16) West, Philip W., Patricia Folse, and Dean Montgomery.
Application of flame spectrophotometry to water analysis. Determination of sodium, potassium, and calcium. Anal. Chem. 22:667. 1950.

INFLUENCE OF CERTAIN CATIONS ON THE INTENSITIES OF SPECTRAL EMISSIONS OBSERVED IN FLAME EXCITATION

by

ROBERT DUNNING WEAVER

A. B., Blackburn College, 1952

AN ABSTRACT OF A THESIS

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This abstract summarizes research performed to determine the applicability of a flame spectrophotometric method to the determination of several elements obtained from plant ash. The elements studied and the wave lengths used were sodium, 589 mu; potassium, 768 mu; calcium, 622 mu; magnesium, 371 mu; boron, 548 mu; cobalt, 352.7 mu; copper, 324.8 mu; iron, 372 mu; and manganese, 403.4 mu. The instrument used was the Beckman Model DU Spectrophotometer employing a Model 9200 flame attachment. A photomultiplier tube and oxy-acetylene flame were used exclusively to obtain the interference data.

A survey of the literature indicated that interference data were available for the alkali and alkaline earth metals as obtained with various flame instruments, and that the magnitude and occurrence of interference is partially dependent upon the instrument used. Less information was found for the remainder of the elements under consideration, however, there were data available indicating that interference between these ions might occur. Information was found indicating that anion interferences might occur if more than one anion were present. For this reason, the data were obtained in the presence of the chloride ion, except in the cases of iron and boron, where ferrous ammonium sulfate and boric acid were used.

Interference data for the ions considered were obtained with instrument parameters adjusted to reduce to a minimum the extent and occurrence of interference. The ions were investigated in two groups: the major group composed of sodium, potassium, calcium, and magnesium,

and the minor group consisting of the remainder. The interference data presented are based upon measurement of the effect upon one ion by the remainder of the ions in its group.

Results of the investigation indicate that, of the major group, calcium and magnesium mutually interfere. Of the minor group, iron and manganese were found to interfere with the determination of the remainder of the ions of the group and with each other. Interference of boron upon manganese determination was also observed. The minimum concentrations of the ions which might be determined with a standard deviation of ten percent were found to be: manganese, 2 ppm; copper, 6 ppm; cobalt, 12 ppm; boron, 14 ppm; and iron, 23 ppm.

On the basis of the data presented, it was suggested that the method of flame analysis of plant ash include a division of the ions into the major group and into two minor groups, one containing iron and manganese and the other boron, cobalt, and copper.